

PATENT ABSTRACTS OF JAPAN

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(71)Applicant : SUMITOMO BAKELITE CO LTD

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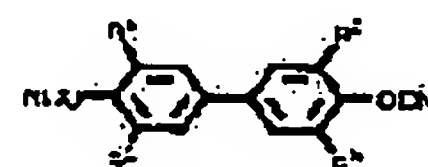
(72)Inventor : TOBISAWA AKIHIKO

(54) HEAT RESISTANT RESIN COMPOSITION, PREPREG USING THE SAME AND LAMINATE

(57)Abstract:

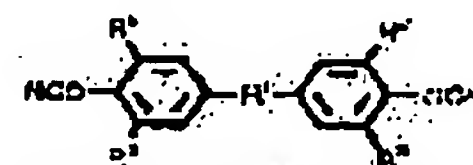
PROBLEM TO BE SOLVED: To obtain a resin composition excellent in heat resistance, dielectric characteristics and water absorption by using a cyanate resin together with a phenol aralkyl epoxy resin or a biphenyl aralkyl epoxy resin, a prepreg and a laminate obtained from the prepreg.

SOLUTION: This heat resistant resin composition comprises (A) a cyanate resin or its prepolymer expressed by general formula (I) and (B1) a biphenyl aralkyl epoxy resin expressed by general formula (II) or (B2) a phenol aralkyl epoxy resin expressed by general formula (III) as essential ingredients.

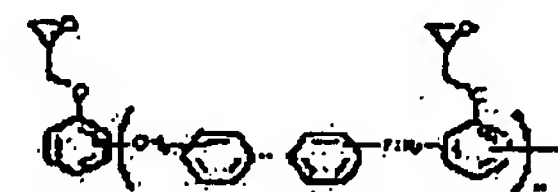


又は

(I)

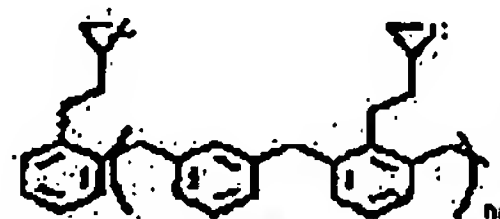


R1, R2はアルキル基、アリーール基
R3, R4はHまたは II, アルキル基、アリーール基



nは1以上の整数

(III)



nは1以上の整数

(IV)

LEGAL STATUS

[Date of request for examination]

06.04.2004

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AN 2002:802531 HCAPLUS
 DN 137:312028
 ED Entered STN: 23 Oct 2002
 TI Heat-resistant resin composition, prepreg and laminate therewith
 IN Tobisawa, Akihiko
 PA Sumitomo Bakelite Co., Ltd., Japan
 SO Jpn. Kokai Tokkyo Koho, 5 pp.
 CODEN: JKXXAF
 DT Patent
 LA Japanese
 IC ICM C08L079-00
 ICS B32B015-08; C08J005-24; C08L063-00; H05K001-03
 CC 38-3 (Plastics Fabrication and Uses)
 FAN.CNT 1

	PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
PI	JP 2002309085	A	20021023	JP 2001-115584	20010413 <--
	JP 2006307227	A	20061109	JP 2006-134981	20060515
PRAI	JP 2001-115584	A3	20010413		

AB The composition comprises (a) (alkylene) bisphenyl dicyanates and (b) biphenyl aralkyl epoxy resins or phenol aralkyl epoxy resins. Impregnating a 55% di-Me cellosolve varnish containing bisphenol A cyanate resin (trimerized ratio 405, B 40) 70, biphenyl aralkyl epoxy resin (NC 3000S) 30, Co acetylacetonate 0.1 part onto a glass fabric, drying 5 min at 150°, stacking 6 resulting prepregs, sandwiching with 2 Cu foils, and hot pressing gave a Cu foil-clad laminate showing water absorption 0.13%, peel strength 1.6, dielec. ratio (1 MHz) 3.9, and normal solder heat resistance.

ST heat resistant resin prepreg laminate; biphenyl aralkyl epoxy resin copper laminate; phenol aralkyl epoxy resin prepreg laminate

IT Laminated plastics, uses
 RL: PRP (Properties); TEM (Technical or engineered material use); USES (Uses)
 (copper-clad; heat-resistant epoxy resin composition for laminates with low dielec. ratio and water absorption)

IT Phenolic resins, uses
 RL: PRP (Properties); TEM (Technical or engineered material use); USES (Uses)
 (epoxy; heat-resistant epoxy resin composition for laminates with low dielec. ratio and water absorption)

IT Heat-resistant materials
 (heat-resistant epoxy resin composition for laminates with low dielec. ratio and water absorption)

IT Epoxy resins, uses
 RL: PRP (Properties); TEM (Technical or engineered material use); USES (Uses)
 (phenolic; heat-resistant epoxy resin composition for laminates with low dielec. ratio and water absorption)

IT 471879-51-3P 471879-52-4P 471879-53-5P
 RL: IMF (Industrial manufacture); TEM (Technical or engineered material use); PREP (Preparation); USES (Uses)
 (heat-resistant epoxy resin composition for laminates with low dielec. ratio and water absorption)

DERWENT-ACC-NO: 2004-194148

DERWENT-WEEK: 200709

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TITLE: Heat resistant resin composition comprising cyanate resin and biphenylaralkyl epoxy resin, useful as a material for preparing a printed circuit substrate

PATENT-ASSIGNEE: SUMITOMO BAKELITE CO LTD[SUMB]

PRIORITY-DATA: 2001JP-0115584 (April 13, 2001)

PATENT-FAMILY:

PUB-NO	PUB-DATE	LANGUAGE	PAGES	MAIN-IPC
<u>JP 2002309085 A</u>	October 23, 2002	N/A	005	C08L 079/00

APPLICATION-DATA:

PUB-NO	APPL-DESCRIPTOR	APPL-NO	APPL-DATE
JP2002309085A	N/A	2001JP-0115584	April 13, 2001

INT-CL (IPC): B32B015/08, C08J005/24, C08L063/00, C08L079/00, H05K001/03

RELATED-ACC-NO: 2007-086212

ABSTRACTED-PUB-NO: JP2002309085A

BASIC-ABSTRACT:

NOVELTY - A novel heat resistant resin composition (I) comprising a cyanate resin or its polymer and; biphenylaralkyl epoxy resin; or phenolaralkylepoxy resin.

DETAILED DESCRIPTION - A novel heat resistant resin composition (I) comprising a cyanate resin or its polymer and; biphenylaralkyl epoxy resin; or phenolaralkylepoxy resin. (A) is represented by formula (I).

R1 = alkyl, aryl;

R2, R3 = H, alkyl, aryl

(B1) is represented by formula (II), (B2) is represented by formula (III).

m, n = integer 1 or more.

USE - (I) is useful as a material for preparing a printed circuit substrate, prepregs prepared from (I) are lapped and pressed at 150-200 deg. C to obtain a printed circuit substrate.

ADVANTAGE - (I) gives printed circuit substrate with good heat resistance, a low dielectric constant and low moisture absorption.

CHOSEN-DRAWING: Dwg.0/0.

TITLE-TERMS: HEAT RESISTANCE RESIN COMPOSITION COMPRISE CYANATE RESIN EPOXY
RESIN USEFUL MATERIAL PREPARATION PRINT CIRCUIT SUBSTRATE

DERWENT-CLASS: A21 A26 A85 L03 P73 V04 X12

CPI-CODES: A05-A01E2; A08-D04A; A12-E07A; L03-H04E1;

EPI-CODES: V04-R07L; X12-E02B;

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the resin constituent and prepreg which were excellent in thermal resistance and were excellent in dielectric characteristics, and a laminate. Especially, it is used suitable for the application of the circuit board for RFs.

[0002] As for information management systems, such as a note type personal computer and a cellular phone, the miniaturization is called for. Also in the printed wired board in which electronic parts, such as LSI, are carried, the demand of the formation of small lightweight is strong. It is required to make wiring width of face small for the formation of small lightweight or to make the diameter of a through hole small and to make plating thickness thin. If plating thickness is made thin, there will be a possibility that a plating crack may occur, at the time of a thermal shock, and thermal resistance will be required at it. Moreover, improvement in the speed of these crises for information processing is also demanded simultaneously, and the CPU clock frequency is high. Therefore, improvement in the speed of signal velocity of propagation is demanded, and it is needed that they are a dielectric constant advantageous to improvement in the speed and the low printed circuit board of a dielectric dissipation factor.

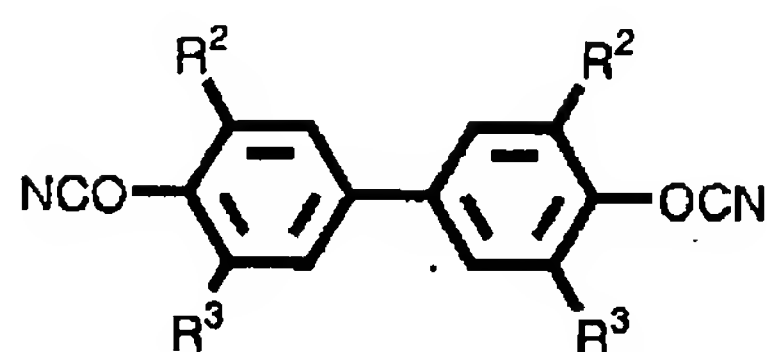
[0003] Cyanate resin is used as resin which was excellent in thermal resistance and was excellent in dielectric characteristics (for example, JP,8-8501,A). Since the large reaction radical of polarization of a hydroxyl group etc. does not arise by the hardening reaction, cyanate resin is dramatically excellent in dielectric characteristics. However, since many nitrogen atoms are included, there is a fault with high water absorption.

[0004]

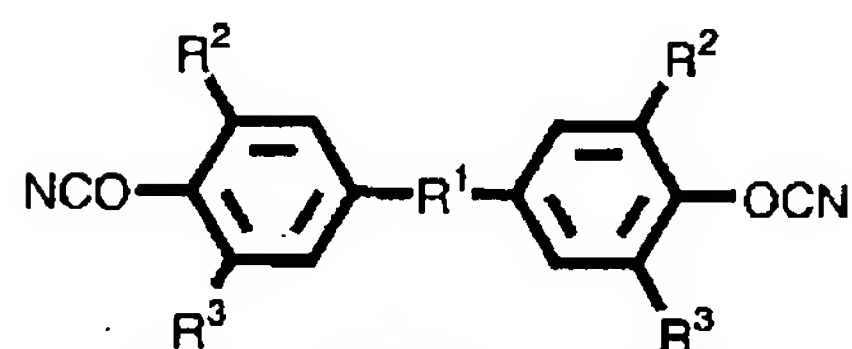
[Problem(s) to be Solved by the Invention] That such a problem should be solved, as a result of examination, it is made and this invention offers the laminate obtained from a resin constituent, prepreg, and prepreg excellent in thermal resistance, dielectric characteristics, and water absorption by using together cyanate resin, a phenol aralkyl epoxy resin, or a biphenyl aralkyl epoxy resin.

[0005]

[Means for Solving the Problem] This invention is the cyanate resin expressed with the (1) (A) following general formula (I) or its prepolymer, and [Formula 3].



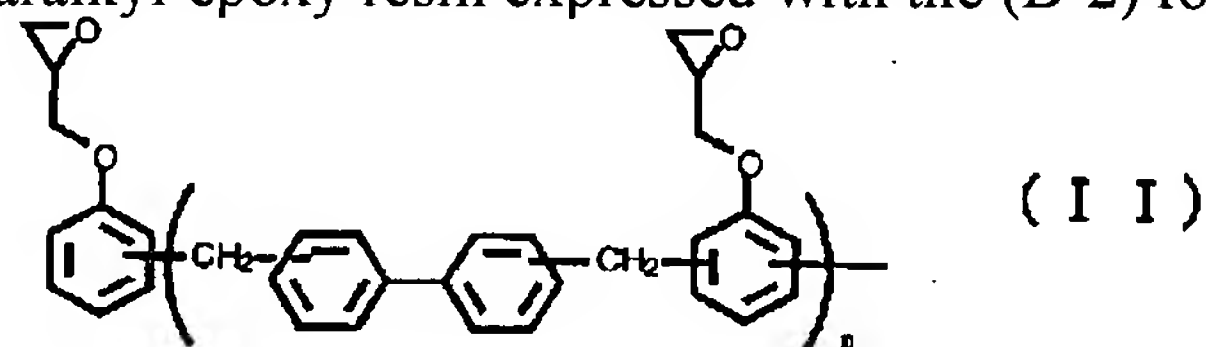
又は (I)



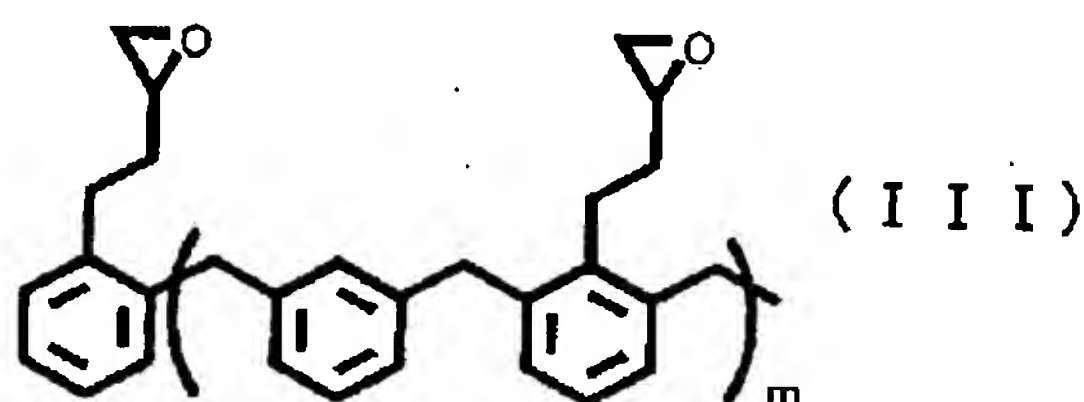
R₁はアルキル基、アリール基

R₂、R₃は -H、アルキル基、アリール基

(B1) The biphenyl aralkyl epoxy resin expressed with the following general formula (II), or the phenol aralkyl epoxy resin expressed with the (B-2) following general formula (III) [** 4]



nは1以上の整数



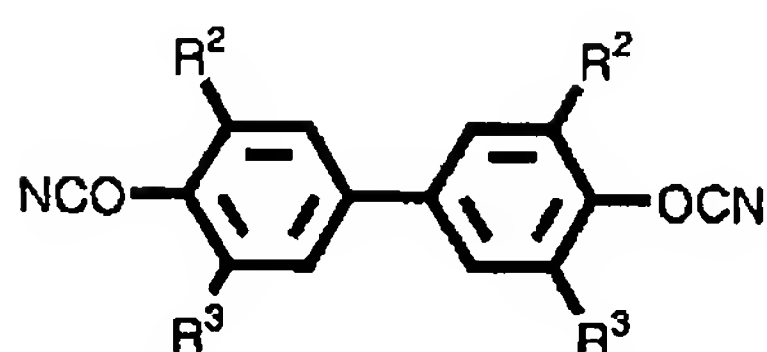
mは1以上の整数

the fire-resistant laminate characterized for the prepreg characterized by coming to carry out impregnation of the heat-resistant-resin constituent and the resin constituent given in (2) ** (1) term which are characterized by coming to contain as an indispensable component to a base material, and prepreg given in (3) ** (2) term by one sheet or coming to carry out two or more sheet superposition heating application of pressure, or copper clad laminate -- it comes out.

[0006]

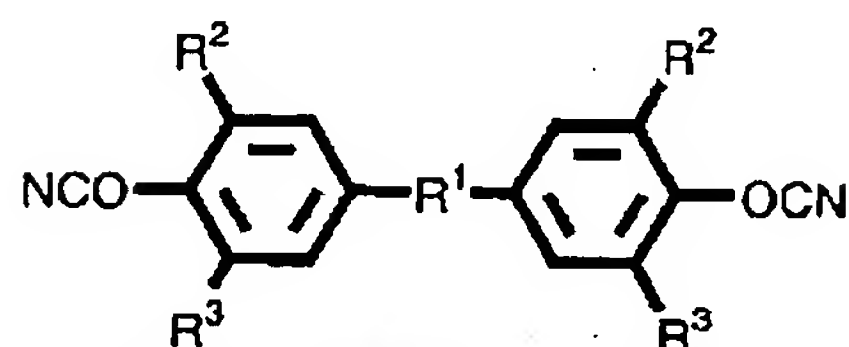
[Embodiment of the Invention] The cyanate resin of the (A) component used by this invention is shown by the following general formula (I).

[Formula 5]



又は

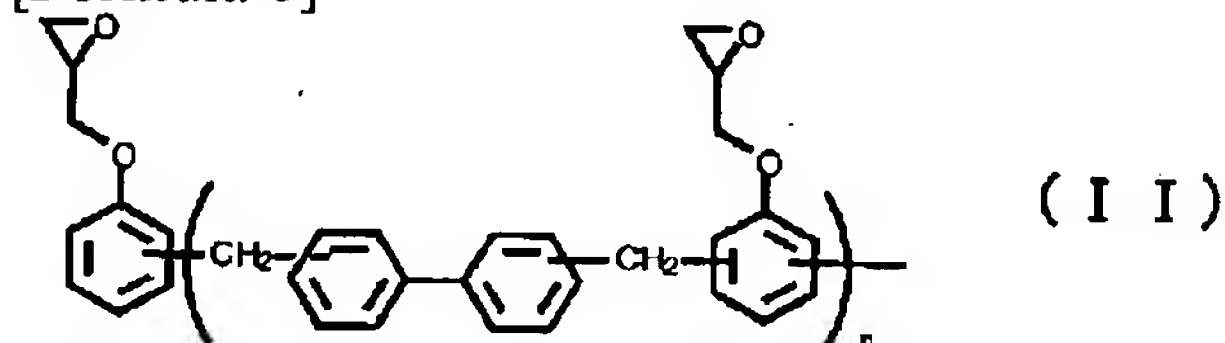
(I)

 R_1 はアルキル基、アリール基 R_2 、 R_3 は -H、アルキル基、アリール基

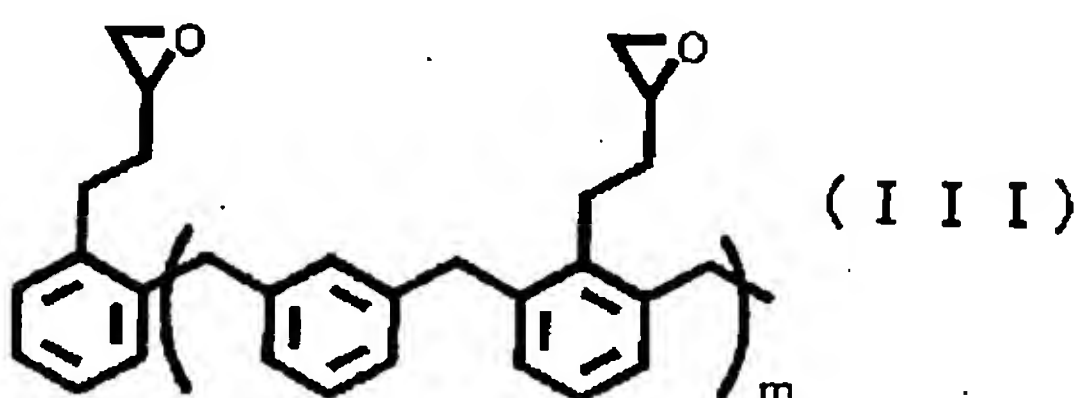
Moreover, in order that what prepolymer-ized the cyanate resin which has this general formula may adjust a moldability and a fluidity, it is used preferably, and it is contained in the (A) component of this invention. Prepolymer-ization is performed by usually carrying out heating fusion. A prepolymer means the thing of 20 - 50% of rates of 3 quantification by this invention. It can ask for the rate of 3 quantification using infrared-spectroscopic-analysis equipment. In addition, what prepolymer-ized cyanate resin and cyanate resin may be used together. Cyanate resin has desirable 50 - 80 weight section among the resinous principle 100 weight section. In under 50 weight sections, if the solder thermal resistance of 260 degrees C is not enough and exceeds 80 weight sections, water absorption gets worse and is not desirable. The alkyl group of R_1 of the cyanate resin in this invention has desirable carbon numbers 1-6, and, as for a carbon number, 2-6 are [an aryl group] desirable. Moreover, similarly, the alkyl group of R_2 has desirable carbon numbers 1-4, and carbon numbers 1-3 of an aryl group are desirable.

[0007] The biphenyl aralkyl resin of a component used by this invention (B1) is shown by the following general formula (II). Moreover, the phenol aralkyl epoxy resin of the (B-2) component is shown by the following general formula (III).

[Formula 6]



(I I)

 n は1以上の整数

(I I I)

 m は1以上の整数

A phenol aralkyl epoxy resin or a biphenyl aralkyl epoxy resin has desirable 20 - 50 weight section among the resinous principle 100 weight section. In under 20 weight sections, if the reduction in water absorption is not enough and exceeds 50 weight sections, the solder thermal resistance of 260 degrees C gets worse and is not desirable. It is desirable also in both at the point that weight per epoxy equivalent

is [a biphenyl aralkyl epoxy resin] large, and the effectiveness of the reduction in water absorption is large. Moreover, as for n of biphenyl aralkyl resin, 2-7 are desirable at this invention in respect of the solder thermal resistance which is 260 degrees C. There is an inclination for crosslinking density to fall that n is less than two, the solder thermal resistance in 260 degrees C may get worse, and if 7 is exceeded, compatibility with cyanate resin may get worse. Moreover, as for m of a phenol aralkyl epoxy resin, 2-7 are desirable especially in respect of the solder thermal resistance which is 260 degrees C. There is an inclination for crosslinking density to fall that m is less than two, the solder thermal resistance in 260 degrees C may get worse, and if 7 is exceeded, compatibility with cyanate resin may get worse.

[0008] As mentioned above, although cyanate resin produces a triazine ring by the hardening reaction, since the triazine ring is excellent in symmetric property, polarization is small and dielectric characteristics are dramatically excellent. Furthermore, since a triazine ring is the upright structure containing nitrogen, it has the description excellent in fire retardancy. However, since cyanate resin has high nitrogen content, it has a fault with high water absorption. Although there is the approach of adding low water absorption resin, such as an elastomer and dicyclopentadiene resin, in order to reduce water absorption, these resin has the fault which is easy to burn. In this invention, in order to solve this problem, a phenol aralkyl epoxy resin or a biphenyl aralkyl epoxy resin is used together to cyanate resin. A phenol aralkyl epoxy resin and a biphenyl aralkyl epoxy resin have large weight per epoxy equivalent, and since the epoxy group concentration in a hardened material becomes small, they are excellent in dielectric characteristics. Moreover, hydrophobicity of water absorption is highly low by the benzene ring in a molecule. Moreover, since it is easy to carbonize benzene ring content highly, a phenol aralkyl epoxy resin and a biphenyl aralkyl epoxy resin do not worsen the burning resistance which was [that it is hard to burn] excellent in cyanate resin. Furthermore, in order that an epoxy group may react with a cyanate radical, since it is incorporable into a resin frame, it does not reduce the thermal resistance which was excellent in cyanate resin.

[0009] As a base material used by this invention, a fabric or a non-woven fabric etc. which makes it a component except a glass fabric, a glass non-woven fabric, or glass is mentioned. A glass cloth is desirable in respect of reinforcement and water absorption also in these base materials.

[0010] An impregnation spreading facility etc. is used for the approach of carrying out impregnation of the resin constituent obtained by this invention to a base material. In this invention, in case it sinks into a base material, it is desirable to use it in the form of the varnish which usually dissolved in the solvent in respect of impregnating ability. Although it is desirable to show good solubility to a presentation as for the solvent used, a poor solvent may be used in the range which does not do an adverse effect. A methyl ethyl ketone, a cyclohexanone, etc. are mentioned as a solvent in which good solubility is shown.

Prepreg can be obtained by carrying out impregnation of the varnish obtained by dissolving the resin constituent of this invention in a solvent to a base material, and drying it at 80-200 degrees C.

[0011] Heating application of pressure of the prepreg obtained by this invention can be carried out at one sheet or two or more sheet pile doubling, and 150-200 degrees C, and a laminate or copper clad laminate can be obtained.

[0012] Although the resin constituent of this invention contains the cyanate resin, phenol aralkyl epoxy resin, or biphenyl aralkyl epoxy resin mentioned above as an indispensable component, in the range which is not contrary to the object of this invention, adding the component of other resin, a hardening accelerator, a coupling agent, a flame retarder, and others does not interfere. If a bromination epoxy resin is used, since an epoxy group and a cyanate radical can react and a flame retarder can be incorporated into a resin frame as a flame retarder, the property of resin is not worsened and it is desirable. As a hardening accelerator, copper content compounds, such as zinc content compounds, such as cobalt content compounds, such as cobalt acetylacetonato and naphthenic-acid cobalt, a zinc chloride, and zinc naphthenate, and a copper chloride, are desirable.

[0013]

[Example] (Example 1) Dimethyl Cellosolve was added to the bisphenol A cyanate resin (thing and 40% of rates of 3 quantification, Ciba-Geigy make B-40) 70 weight section, the biphenyl aralkyl epoxy resin

(weight-per-epoxy-equivalent 280, NC[by Nippon Kayaku Co., Ltd.]- 3000 S) 30 weight section, and the cobalt acetylacetonate complex 0.10 weight section, and the varnish was adjusted so that it might become 55 % of the weight of nonvolatile matter concentration. [which were prepolymer-ized] Carried out 80 weight sections impregnation to the glass fabric (0.18mm [in thickness], Nitto Boseki Co., Ltd. make) 100 weight section by varnish solid content, it was made to dry at a 150-degree C dryer furnace for 5 minutes using this varnish, and the prepreg of 44.4% of resin contents was created. The six above-mentioned prepregs were piled up, up and down, electrolytic copper foil with a thickness of 35 micrometers was performed at pressure 40 kgf/cm² and the temperature of 200 degrees C, heating pressing was performed at 220 degrees C in piles, for 60 minutes for 120 minutes, and double-sided copper clad laminate with a thickness of 1.2mm was obtained.

[0014] (Examples 2-5 and examples 1-3 of a comparison) By the combination formula shown in a table 1, double-sided copper clad laminate was created by the same approach as an example 1 except [all] this.

[0015] About the obtained copper clad laminate, fire retardancy, solder thermal resistance, the Peel reinforcement, and water absorption were measured. About solder thermal resistance, the Peel reinforcement, and water absorption, it measured according to JIS C 6481, and solder thermal resistance investigated the existence of the abnormalities of the appearance after being immersed in a 260-degree C solder tub for 120 seconds, after performing moisture absorption processing of boiling 2 hours. Fire retardancy evaluated the sample of 1mm thickness by normal beam testing according to UL-94 specification. A glass transition point is REOMETO Rix make. It measured using RDS-7700 on the programming rate of 3 degrees C / min, and the frequency of 1Hz. Measurement of a dielectric constant and a dielectric dissipation factor was performed according to JIS C 6481, and electrostatic capacity with a frequency of 1MHz was measured and calculated. An assessment result is shown in a table 1. Each copper clad laminate shown in an example has a dielectric constant and a low dielectric dissipation factor, and it turns out that it excels in thermal resistance, solder thermal resistance, and water absorption.

[0016]

[A table 1]

項目	実施例1	実施例2	実施例3	実施例4	実施例5
配合量 (重量部)					
シアネート樹脂 ¹⁾	70	50	50	90	40
ビフェニルアラキルエポキシ樹脂 ²⁾	30	30		10	60
フェノールアラキルエポキシ樹脂 ³⁾			30		
臭素化エポキシ樹脂 ⁴⁾		20	20		
Co(acac) ₃ ⁵⁾	0.10	0.08	0.08	0.10	0.10
特性					
ガラス転移温度(°C)	195	185	198	210	170
誘電率(1MHz)	3.9	3.8	3.8	3.9	3.8
誘電正接(1MHz)	0.005	0.007	0.008	0.007	0.007
半田耐熱性	異常なし	異常なし	異常なし	異常なし	異常なし
吸水率	0.13	0.12	0.13	0.18	0.10
ピール強度	1.6	1.4	1.4	1.6	1.3

[0017]

[A table 2]

項目	比較例1	比較例2	比較例3
配合量 (重量部)			
シアネート樹脂 ¹⁾	100	80	50
フェノールノボラックエポキシ樹脂 ⁶⁾			30
臭素化エポキシ樹脂 ⁴⁾		20	20
Co(acac) ₃ ⁵⁾	0.16	0.08	0.08
特性			
ガラス転移温度(°C)	230	210	201
誘電率(1MHz)	4.0	4.0	4.2
誘電正接(1MHz)	0.015	0.015	0.018
半田耐熱性	異常なし	異常なし	異常なし
吸水率	0.25	0.21	0.24
ピール強度	1.6	1.3	1.3

[0018] Notes (1) bisphenol A cyanate of a table (prepolymer-izing: 40% of rates of 3 quantification, trade name: Ciba-Geigy make B-40)

(2) Biphenyl aralkyl epoxy resin (weight per epoxy equivalent 280, a trade name: NC[by Nippon Kayaku Co., Ltd.]- 3000 S)

(3) Phenol aralkyl epoxy resin (weight per epoxy equivalent 235, a trade name: E-XL[by Mitsui Chemicals, Inc.]-3L)

(4) Bromination epoxy resin (weight per epoxy equivalent 400, 48% of bromination rates, Epiclon 153 by Dainippon Ink & Chemicals, Inc.)

(5) Cobalt acetylacetonato (6) phenol novolak epoxy resin (weight per epoxy equivalent 190, Epiclon N-770 by Dainippon Ink & Chemicals, Inc.)

[0019]

[Effect of the Invention] The heat-resistant-resin constituent of this invention has the property which has high thermal resistance, and has the property that a dielectric constant is low, and was excellent in water absorption, when applied to a printed wired board ingredient. Therefore, the optimal resin constituent for the printed wired board of the crisis for small information processing will be offered from now on.

[Translation done.]

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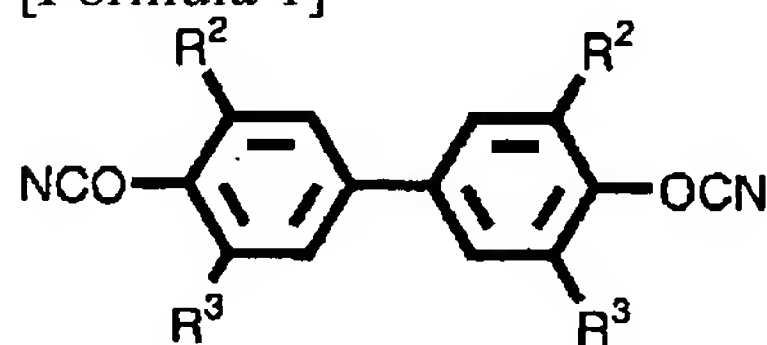
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CLAIMS

[Claim(s)]

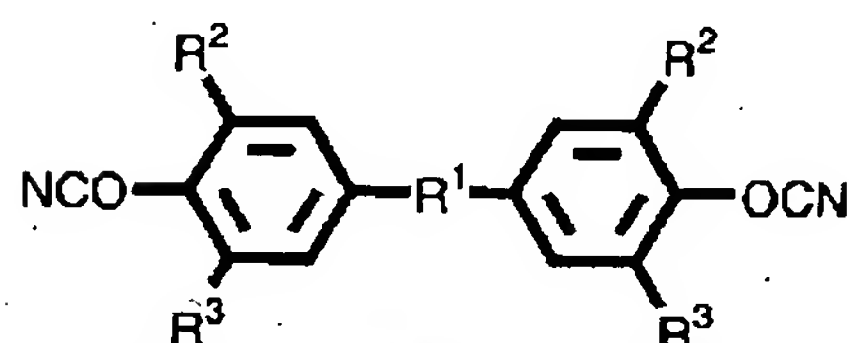
[Claim 1] (A) The cyanate resin expressed with the following general formula (I) or its prepolymer, and

[Formula 1]

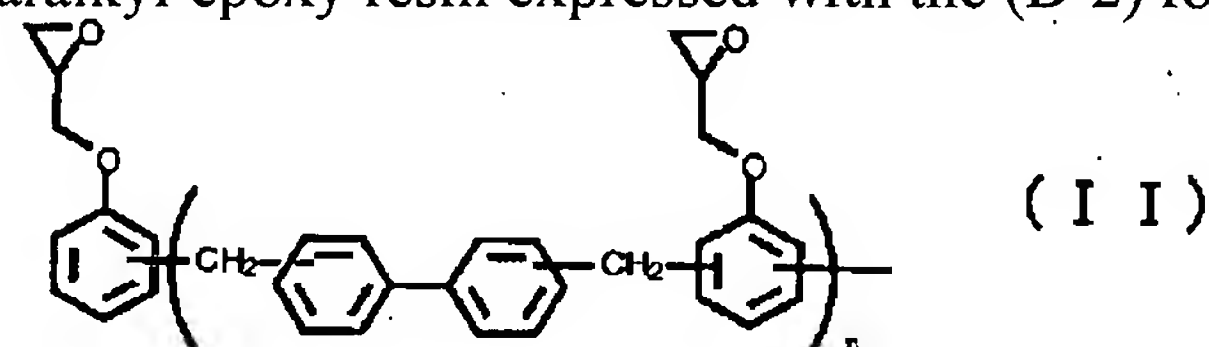


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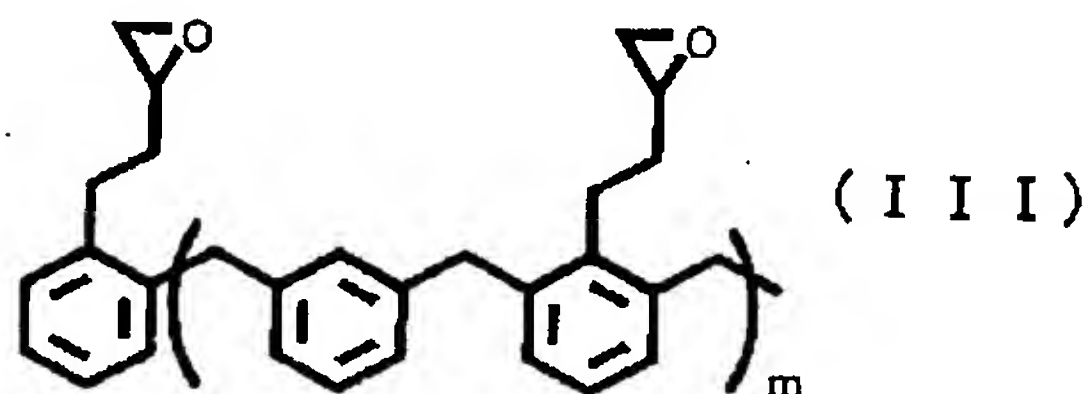
(I)

 R_1 はアルキル基、アリール基 R_2 、 R_3 は -H、アルキル基、アリール基

(B1) The biphenyl aralkyl epoxy resin expressed with the following general formula (II) or the phenol aralkyl epoxy resin expressed with the (B-2) following general formula (III), [Formula 2]



(I I)

 n は1以上の整数

(I I I)

 m は1以上の整数

The heat-resistant-resin constituent characterized by coming to contain as an indispensable component.
[Claim 2] Prepreg characterized by coming to carry out impregnation of the resin constituent according to claim 1 to a base material.

[Claim 3] The fire-resistant laminate or copper clad laminate characterized for prepreg according to claim 2 by one sheet or coming to carry out two or more sheet superposition heating application of pressure.

[Translation done.]